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REACTIONS OF METAL-METAL TRIPLE BONDS. 7. ADDITION OF THE MALO6--ETC(U)

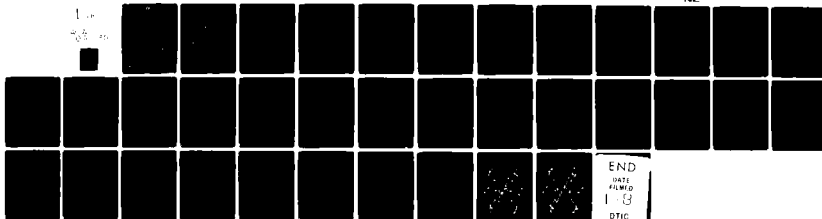
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REACTIONS OF METAL-METAL TRIPLE BONDS. 7. ADDITION OF THE
HALOGENS (Cl_2 , Br_2 and I_2) AND DIISOPROPYLPEROXIDE TO
HEXAISOPROPOXYDIMOLYBDENUM (M-M). DINUCLEAR OXIDATIVE-
ADDITION REACTIONS ACCOMPANIED BY METAL-METAL BOND
ORDER CHANGES FROM THREE TO TWO TO ONE

10 by
Malcolm H. Chisholm, Charles C. Kirkpatrick and John C. Huffman

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<p>Mo₂(OPrⁱ)₆ (M≡M) and PrⁱOOPrⁱ react in hydrocarbon solvents, at room temperatures and in the dark, to give the previously characterized compound Mo₂(OPrⁱ)₈ (M=M). Mo₂(OBu^t)₆ (M≡M) fails to react with either PrⁱOOPrⁱ or Bu^tOOBu^t and Mo₂(OPrⁱ)₆ and Bu^tOOBu^t do not react under similar conditions. A reaction</p>		

pathway involving an initial association reaction is proposed:

$$\text{Mo}_2(\text{OR})_6 + \text{ROOR} \rightleftharpoons \text{Mo}_2(\text{OR})_6(\text{ROOR}) \longrightarrow \text{Mo}_2(\text{OR})_8 \cdot \text{Mo}_2(\text{OPr}^i)_6$$
 reacts with each of the halogens (Cl_2 , Br_2 and I_2) to give $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ (M-M) compounds ($\text{X} = \text{Cl}$, Br and I). These reactions proceed via intermediates, probably $\text{Mo}_2(\text{OPr}^i)_6\text{X}_2$ compounds, which are labile toward disproportionation to give $\text{Mo}_2(\text{OPr}^i)_6$ and $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds. The compounds $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ are thermally unstable and moisture sensitive. In vacuo or under a nitrogen atmosphere they decompose slowly at room temperature by the elimination of isopropyl halides. X-ray studies on the chloro and bromo compounds show that both compounds contain central $\text{Mo}_2\text{O}_6\text{X}_4$ units that have virtual D_{2h} symmetry. Each molybdenum atom is in a distorted octahedral environment formed by a pair of cis terminal halide ligands, a pair of trans terminal OPr^i ligands and a pair of cis-bridging OPr^i ligands. There are planar $\text{Mo}_2(\mu\text{-O})_2\text{X}_4$ units and the M-M distance in both is 2.73 \AA , which, together with other characterization data, are indicative of Mo-to-Mo single bonds. These findings are compared with earlier work. Crystal data are as follows for $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$: $a = 20.722(6) \text{ \AA}$, $b = 9.617(2) \text{ \AA}$, $c = 14.747(4) \text{ \AA}$, $\beta = 96.02(1)^\circ$, $V = 2922.6(1) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd.}} = 1.578 \text{ g cm}^{-3}$ with space group $\text{P2}_1/\text{a}$, for $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4 \cdot 1/2\text{C}_7\text{H}_8$: $a = 15.204(5) \text{ \AA}$, $b = 12.849(5) \text{ \AA}$, $c = 10.535(3) \text{ \AA}$, $\beta = 120.76(1)^\circ$, $V = 1768.6(1) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd.}} = 1.638 \text{ g cm}^{-3}$ with space group $\text{P2}_1/\text{a}$.

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INTRODUCTION

In mononuclear transition metal chemistry, the term oxidative-addition² is often used to describe reactions in which both the oxidation number and coordination number of the metal are increased by two. The microscopic reverse reaction is called reductive elimination, and the two complementary reactions are incorporated into numerous catalytic cycles, involving especially the group 8 transition elements.² We have speculated³ that dinuclear compounds of the transition elements containing metal-to-metal triple bonds⁴ might also enter into these types of reactions and that M-M bond order changes would occur. In this paper we describe some simple addition reactions involving $\text{Mo}_2(\text{OPr}^i)_6$ ($\text{M}\equiv\text{M}$)⁵ in which the Mo-to-Mo bond order is changed in a stepwise manner from three to two to one.

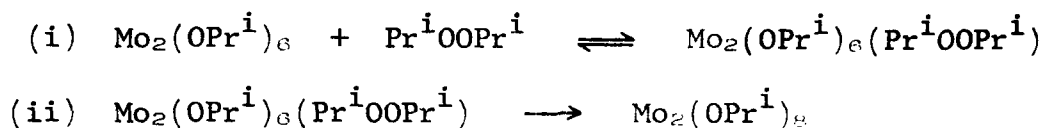
RESULTS AND DISCUSSION

$\text{Mo}_2(\text{OPr}^i)_6 + \text{Pr}^i\text{OOPr}^i$. Hydrocarbon solutions of $\text{Mo}_2(\text{OPr}^i)_6$ are pale yellow and upon addition of Pr^iOOPr^i at room temperature quickly turn green-blue. In the presence of a five-fold excess of the diisopropylperoxide, $\text{Mo}_2(\text{OPr}^i)_6$ is formed virtually quantitatively within 12 h at room temperature. The latter compound may be isolated by merely stripping the solvent and excess diisopropylperoxide and can be purified by vacuum sublimation.⁶ The reaction is accelerated by heat and light, though the latter is not required at room temperature. Below room temperature the reaction is slow and does not go to completion within a period of days. When the reaction was carried out in a sealed tube within the cavity of an esr spectrometer, no signals were detected.

The addition of Bu^tOObu^t to hydrocarbon solutions of either $\text{Mo}_2(\text{OPr}^i)_6$ or $\text{Mo}_2(\text{OBu}^t)_6$ results in color changes but little reaction evidently occurs at ambient temperatures since the $\text{Mo}_2(\text{OR})_6$ compounds are recovered upon sublimation of the solids obtained by stripping the solvent and excess Bu^tOObu^t . In a similar experiment Pr^iOOPr^i was added to $\text{Mo}_2(\text{OBu}^t)_6$: again only $\text{Mo}_2(\text{OBu}^t)_6$ was recovered.

We believe that steric factors are important in determining the rates of these addition reactions and that the reactivity order $\text{Mo}_2(\text{OPr}^i)_6 > \text{Mo}_2(\text{OBu}^t)_6$ which parallels that observed toward Lewis bases,⁵ aryl azides⁷ and molecular oxygen,⁸ may be rationalized by the requirement that the

dialkylperoxide must coordinate to the dimetal center before O-O bond cleavage and oxidative addition is achieved.

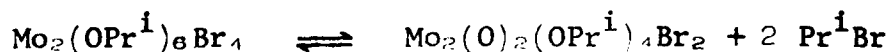


$\text{Mo}_2(\text{OPr}^i)_6 + \text{X}_2$ (X = Cl, Br and I). $\text{Mo}_2(\text{OPr}^i)_6$ in CCl_4 reacts rapidly with Cl_2 and Br_2 to give orange crystalline solids $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$, where X = Cl and Br, respectively. In hexane $\text{Mo}_2(\text{OPr}^i)_6$ and I_2 react to give $\text{Mo}_2(\text{OPr}^i)_6\text{I}_4$ as a brown solid. The rate of addition follows the order $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$. When only 1 equivalent of Br_2 is added slowly the solution is initially green but with time turns orange as $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ crystallizes from solution. The solution contains $\text{Mo}_2(\text{OPr}^i)_6$. Addition of I_2 (1 equiv) to $\text{Mo}_2(\text{OPr}^i)_6$ in hexane gives an intense green solution from which hexane soluble green crystals can be isolated. This compound, believed to be $\text{Mo}_2(\text{OPr}^i)_6\text{I}_2$, is currently the subject of further studies.

Physicochemical Properties of $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ Compounds
(X = Cl, Br, I). All the compounds are moisture sensitive and thermally unstable. They slowly decompose in vacuo and under nitrogen at room temperature by the elimination of isopropyl halides. The resultant black molybdenum containing residues are insoluble in all common organic solvents and have not been characterized. The $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds are insoluble in hexane and other aliphatic hydrocarbons but

they are appreciable soluble and can be recrystallized from toluene and benzene solutions. In the mass spectrometer there were no molybdenum containing ions: the spectra showed intense Pr-X^+ ions. When samples were heated in vacuo to 60°C isopropyl halides were evolved and were identified by ^1H NMR spectroscopy. Cryoscopic molecular weight determinations were carried out on both the chloro and bromo compounds: in both instances low molecular weights were obtained. We attribute this to the instability of the compounds and to their ready decomposition by the elimination of Pr^iX . The ^1H NMR spectra of all three compounds were similar indicative of two types of OPr^i ligands in the ratio 2:1. The spectra are consistent with the maintenance of the solid state structure in solution and the two types of OPr^i ligands can be assigned to terminal and bridging OPr^i ligands, both of which lie in planes of molecular symmetry. One point of initial concern to us was the anomalous deshielding associated with one of the methyne protons which increased in the order $\text{I} > \text{Br} > \text{Cl}$. As is shown later this can be rationalized by structural considerations.

In order to check whether elimination of Pr^iBr was reversible we prepared $(\text{CD}_3)_2\text{CHBr}$. Addition of $(\text{CD}_3)_2\text{CHBr}$ to a solution of $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ in toluene- d_8 gave no evidence (from ^1H NMR studies) for the reversible reaction shown below.



We conclude that when $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds eliminate Pr^iX , they do so irreversibly. In this and all other respects the $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds appear to be analogous to the tungsten compounds $\text{W}_2(\text{OR})_6\text{Cl}_4$ ($\text{R} = \text{Me}, \text{Et}$ and $n\text{-Pr}$) studied by Brubaker and his coworkers¹⁴ and originally prepared by Klejnot.⁹ On the basis of i.r. studies these authors favored the existence of chloride bridges. We show, however, that for molybdenum there are alkoxy bridges and only terminal halide groups.

Solid State Structures

$\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$. In the crystalline state the compound is composed of discrete molecules of $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$. An ORTEP view of the molecule indicating the coordination geometry and atom numbering scheme is shown in Figure 1. Final atomic coordinates and thermal parameters are given in Table 1. Complete listings of bond distances and angles to non-hydrogen atoms are given in Tables 2 and 3, respectively. Bond distances and angles to hydrogen atoms and non-bonding distances to 3.0 Å are given in the supplementary material.

The central $\text{Mo}_2\text{O}_6\text{Cl}_4$ unit has virtual D_{2h} symmetry. Each molybdenum atom is in a distorted octahedral geometry. There are a pair of cis Mo-Cl groups, a pair of trans-terminal OPr^i ligands and a pair of cis-bridging OPr^i ligands.

$\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$. This compound crystallized with a molecule of solvent (toluene) in the unit cell. The toluene molecule

was disordered and was refined isotropically. All hydrogen atoms (other than those of the solvent molecule) were located and refined. An ORTEP view of the $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ molecule showing the coordination geometry and the atom numbering scheme is shown in Figure 2. Final atomic coordinates and thermal parameters are given in Table 4. Complete listings of bond distances and angles, involving non-hydrogen atoms are given in Tables 5 and 6, respectively.

The central $\text{Mo}_2\text{O}_6\text{Br}_4$ unit has virtual D_{2h} symmetry and a crystallographically imposed center of inversion relating the two halves of the dimer. The $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ molecule has rigorous C_{2h} symmetry.

Remarks on Structure and Bonding in $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ Molecules

The angles subtended at molybdenum to the oxygen and halide atoms in both $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$ and $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ are remarkably similar and deviate little from those required for a regular octahedral set of molybdenum atomic hybrid orbitals. The greatest deviation from linearity for a trans angle occurs for the mutually trans pair of terminal OPr^i ligands. Here the O-Mo-O angle is 118° (averaged) and the distortion bends these bonds away from the center of the molecule. This distortion no doubt results from steric repulsive interactions. Indeed space filling models suggest that steric factors determine the arrangement of the isopropyl groups and thus confine the methyne protons of the bridging

OPr^{i} ligands to the $\text{Mo}_2\text{X}_4\text{O}_2$ plane and bring about abnormally short $\text{CH}\cdots\text{X}$ non-bonding distances, 2.48 Å (average) in $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{Cl}_4$ and 2.59 Å in $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{Br}_4$. It is this short distance that we believe is responsible for producing the anomalous deshielding of the methyne proton resonances of the bridging OPr^{i} ligands which occur at $\delta = 7.90$, 7.44 and 7.21 (δ in ppm relative to Me_4Si) when $\text{X} = \text{I}$, Br and Cl , respectively.

The observed diamagnetic nature of the compounds and the short Mo-to-Mo distances, 2.731(1) Å in $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{Cl}_4$ and 2.739(1) Å in $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{Br}_4$, are consistent with the view that these compounds contain Mo-Mo single bonds. Whenever bridging groups are present it is not possible to distinguish unequivocally between the direct coupling of electron spins (M-M bonding) and indirect coupling through bridges. However, for the $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{X}_4$ compounds the evidence for direct metal-metal bonding is virtually overwhelming.

1. Though Mo-Mo single bonds vary greatly in length depending upon oxidation state number and the character of the ligands present, the distance 2.73 Å is rather a normal value.¹⁰

2. The Mo-Mo distances in $\text{Mo}_2(\text{OPr}^{\text{i}})_6\text{X}_4$ compounds may be compared to the $\text{Mo}\equiv\text{Mo}$ bond distance, 2.222(2) Å, in $\text{Mo}_2(\text{OCH}_2\text{CMe}_3)_6$ ⁵ and the $\text{Mo}=\text{Mo}$ bond distances of 2.498(1) and 2.523(1) Å found in $\text{Mo}_2(\text{OBu}^{\text{t}})_6(\text{CO})$ ¹¹ and $\text{Mo}_2(\text{OPr}^{\text{i}})_6$ ¹², respectively. In both of the latter compounds there are bridging OR ligands.

3. In both $[\text{Mo}(\text{OPr}^{\text{i}})_3(\text{NO})]_2$ ¹² and $[\text{Mo}(\text{OPr}^{\text{i}})_3(\text{NO})(\text{HNMe}_2)]_2$ ¹³

there are planar central $\text{Mo}_2(\mu\text{-O})_2$ groups with Mo-to-Mo distances of 3.335(2) and 3.390(2) Å, respectively. On electronic grounds we have argued that these are non-bonding Mo-to-Mo distances.

4. A comparison with the $[\text{Nb}(\text{OMe})_5]_2$ structure¹⁴ is particularly pertinent. Niobium and molybdenum are sister elements differing only in one valence electron. In the compounds $[\text{Nb}(\text{OMe})_5]_2$ and $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$, the metal atoms are in oxidation state number +5 and in octahedral coordination environments. The metal-oxygen distances are similar and the only major difference concerns the structural parameters of the central $\text{M}_2(\mu\text{-O})_2$ units. For $[\text{Nb}(\text{OMe})_5]_2$ there are two conformers in the unit cell which yield an averaged Nb-to-Nb distance of 3.5 Å and an average Nb-O-Nb angle of 110°. This contrasts with the much shorter Mo-to-Mo distance [2.735 Å (averaged)] and more acute Mo-O-Mo angle (85°) found in the $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ molecules. These structural differences arise because the dimers are of the type $d^0\text{-}d^0$ (Nb-Nb) and $d^1\text{-}d^1$ (Mo-Mo) which correspond to M-M bond orders of zero and one, respectively. The M-M bond in $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ is easily pictured as a σ -bond arising from the overlap of two t_{2g} -type d orbitals which, in an octahedral geometry, have lobes directed in between the oxygen atoms that bridge the two molybdenum atoms.

Aside from the structural evidence of the M-M bond there is chemical evidence for its existence. $[\text{Nb}(\text{OMe})_5]_2$ reacts with pyridine and many other donor molecules¹⁵ to give

mononuclear adducts of the form $\text{Nb}(\text{OMe})_5\text{I}$. On the other hand $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ dissolves in pyridine- d_5 without cleavage of the dimer: the ^1H nmr spectrum is essentially the same as that obtained in toluene- d_6 .

6. Finally in 1969 Cotton¹⁶ noted: "For any particular element it is possible empirically to locate a transition region within the entire range of its known formal oxidation states in which M-M bonding gains ascendancy. With molybdenum the influence of the nature of the bridging ligands is clearly shown by the fact that with oxygen and chlorine the threshold of M-M bonding is reached at different oxidation states. Structural evidence for Mo-Mo bonding in the $\text{Mo}_2(\mu\text{-O})_2$ system is found¹⁷ for the $\text{Mo}(5+)$ anion $\text{Mo}_2(\text{O})_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^{2-}$ whereas both structural¹⁸ and magnetic¹⁹ evidence show that there is no Mo-to-Mo bond in $\text{Mo}_2\text{Cl}_{10}$." The structural characterization of the $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds is thus particularly noteworthy. We now see that for a mixed halide alkoxide of $\text{Mo}(5+)$, through the agency of bridging alkoxide ligands, Mo-Mo bonds are formed.

The last point of interest in the $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ structures concerns the extremely short Mo-O distances, 1.81 Å (averaged) associated with the terminal OPr^i ligands. This is significantly shorter (by 0.06 Å or more) than any other Mo-OR distance yet reported. Indeed these distances are only slightly longer than the oxo-molybdenum distance, 1.801(9) Å, reported²⁰ for the green isomer of $\text{MoOCl}_2(\text{PPhEt}_2)_2$. This distance has

been considered to be a Mo-O double bond distance when compared to shorter distances, ca. 1.69 Å, normally associated with Mo-O triple bonds.²¹ For the $\text{Mo}_2(\text{OPr}^i)_6\text{X}_4$ compounds the short Mo-OR (terminal) distances testify to the ability of the alkoxy ligand to respond to the increased needs of a metal to receive π -electron density as its oxidation state is increased and/or as ligands are replaced by poorer π -donors.²²

CONCLUSIONS

In this work we have shown that oxidative additions to a compound containing a $M\equiv M$ bond can occur with concomitant changes in M-M bond order from three to two and one. Previously we have shown²³ that reductive elimination from a dimolybdenum center can bring about a metal-to-metal bond order change from three to four. The prospects for dinuclear transition metal chemistry³ are thus further emphasized. The generality and/or limitations of such transformations remains to be established, however.

EXPERIMENTAL SECTION

General Procedures. All preparations and operations were carried out under a dry and oxygen-free atmosphere or in vacuo, using standard Schlenk techniques.²⁴ Hexane, toluene and benzene were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, phenylether and sodium. Carbon tetrachloride was distilled over P_2O_5 under a nitrogen atmosphere. Samples were stored and handled in a Vacuum Atmospheres Company Dri Lab system.

NMR spectra were obtained from a Varian Associates XL-100 spectrometer. Infrared spectra were recorded on a Perkin Elmer 273 infrared spectrophotometer. Mass spectra were obtained on an AE1 MS 902 by the method of direct insertion, courtesy of Mr. Peter Cook, Queen Mary College, London.

Materials. $Mo_2(OPr^i)_6$ and $Mo_2(OBu^t)_6$ were prepared as described previously.⁵ Pr^iOOPr^i and Bu^tOObu^t were prepared by reacting CH_3SO_3R ($R = Bu^t$ and Pr^i , respectively) with H_2O_2 in alkaline medium.^{25,26} $CD_3CHBrCD_3$ was prepared by the reaction between PBr_3 and $CD_3CHOHCD_3$. The latter compound was made from the reaction between acetone- d_6 (Merch-Sharp and Dohme) and $LiAlH_4$, followed by acid hydrolysis.

High purity Cl_2 was purchased from Matheson and was

used without further purification. I_2 was purified by sublimation. Solutions of bromine in carbon tetrachloride were standardized by addition of KI followed by titration of the liberated I_2 with standard solutions of $Na_2S_2O_3$.

$Mo_2(OPr^i)_6 + Pr^iOOPr^i$. $Mo_2(OPr^i)_6$ (0.54 g, 0.97 mmol) was dissolved in hexane (50 mL). To this yellow solution Pr^iOOPr^i (0.5 mL, 5.0 mmol) was added. The solution immediately began to turn green, and upon stirring overnight (ca. 12 h) became blue. The solvent was stripped and the remaining solids sublimed at $80^\circ C$, 10^{-3} torr. The 1H NMR spectrum, i.r. spectrum and mass spectrum of the blue sublimate corresponded to that of $Mo_2(OPr^i)_8$. Trace quantities of unreacted $Mo_2(OPr^i)_6$ were detected.

In a similar situation $Mo_2(OPr^i)_6$ and Bu^tOObu^t , and, $Mo_2(OBu^t)_6$ and each of Bu^tOObu^t and Pr^iOOPr^i were found not to react: though the solution took on a green appearance only the $Mo_2(OR)_6$ compounds were recovered upon sublimation.

$Mo_2(OPr^i)_6Cl_4$. $Mo_2(OPr^i)_6$ (0.462 g, 0.85 mmol) was dissolved in CCl_4 (175 mL) in a 500 mL round bottomed flask. Cl_2 (1.70 mmol) was condensed into a Urey tube to provide a pressure of 0.68 Atmos at $22^\circ C$ by way of a calibrated vacuum manifold. The Urey tube was connected to the flask containing the hexane solution of $Mo_2(OPr^i)_6$ under 1 Atmos (nitrogen gas + solvent vapor) by a glass tube fitted with stopcocks. The chlorine gas was then allowed to slowly diffuse toward the

hexane solution of $\text{Mo}_2(\text{OPr}^i)_6$. After 3 days the solution was brown and red-brown crystals had formed at the bottom of the reaction vessel. These were recrystallized from toluene to give red crystals of $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$. The results of several analyses varied considerably, depending largely upon the age of the sample. E.g., Analysis Calcd: C, 31.39; H, 6.15; Cl, 20.61%. Found: C, 25.87; H, 5.67; Cl, 23.13%. Crystals for X-ray studies were freshly prepared, kept cold (ca. -15°C) prior to mounting in the liquid nitrogen boil-off cold stream. Infrared data obtained from a Nujol mull between CsI plates: 260 m, 305 m, 410 m, 435 w, 454 m, 499 s, 596 m, 612 w, 639 s, 728 w, 833 s, 868 s, 897 s, 960 vs, 989 s, 1098 vs, 1134 m, 1169 m, 1262 w, 1310 s, 1320 m and 2900 vs cm^{-1} . ^1H nmr data obtained from toluene- d_8 solutions at 100 MHz, 22°C : δ = 0.94 (d, 12H); 1.73 (d, 6H); 5.58 (septet, 2H) and 7.21 (septet, 1H), $J_{\text{HH}} = 7.0$ Hz. δ in ppm relative to Me_4Si .

Addition of 1 equivalent of Cl_2 to $\text{Mo}_2(\text{OPr}^i)_6$ in CCl_4 gave only a mixture $\text{Mo}_2(\text{OPr}^i)_6$ and $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$ under analogous conditions to those described above. Addition of greater than 2 equivalents of Cl_2 lead to destruction of $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$ and formation of hydrocarbon insoluble products.

$\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$. $\text{Mo}_2(\text{OPr}^i)_6$ (1.161 g, 2.12 mmol) was dissolved in CCl_4 (80 mL). The solution was cooled to 0°C in an ice-bath and a solution of Br_2 in CCl_4 (4.24 mmol of Br_2) was added slowly by syringe. The solution immediately turned green, and then red as an orange precipitate formed. The

solution was stirred and warmed to room temperature and the orange precipitate was collected by filtration and then crystallized from toluene. The results of several elemental analyses were erratic and inconclusive [e.g., anal. calcd. for $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$: C, 24.96; H, 4.89; Br, 36.91%. Found: C, 25.12; H, 4.79; Br, 33.68%]. The crystals for X-ray studies were freshly prepared, kept cold (ca. -15°C) and taken directly from the mother liquor to the point of data collection in the liquid nitrogen boil-off cold stream. The crystals grown from toluene evidently contain toluene in the unit cell. This solvent is lost if the crystals are dried in vacuo, since they then fail to diffract X-rays and they show no evidence of toluene in the infrared, ^1H nmr or mass spectrum. I.r. data obtained from a Nujol mull between CsI plates: 280 w, 328 w, 399 m, 430 w, 445 m, 491 s, 583 m, 597 w, 629 vs, 721 w, 805 m, 823 s, 863 s, 888 s, 895 s, 943 vs, 982 s, 1014 s, 1092 vs, 1130 s, 1161 s, 1259 m, 1316 s, 1367 s and 2940 vs cm^{-1} . ^1H nmr data obtained from toluene- d_6 at 100 MHz, 22°C : δ = 0.91 (d, 12H), 1.55 (d, 6H), 5.68 (septet, 2H) and 7.44 (septet, 1H); J_{HH} = 7.0 Hz. δ in ppm relative to Me_4Si .

Under analogous conditions to those described above the addition of 1 equivalent of Br_2 to $\text{Mo}_2(\text{OPr}^i)_6$ gave green solutions which slowly turned orange as $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ was precipitated from solution. The mother liquor contained only $\text{Mo}_2(\text{OPr}^i)_6$. Addition of greater than 2 equivalents of Br_2 gave only $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ and unreacted Br_2 in the CCl_4 solution.

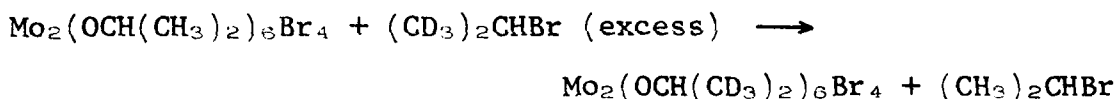
Mo₂(OPrⁱ)₆I₄. Mo₂(OPrⁱ)₆ (0.790 g, 1.44 mmol) was dissolved in hexane (30 mL). To this solution, cooled to ca. 0°C, I₂ (0.531 g, 2.88 mmol) dissolved in hexane (ca. 100 mL) was added dropwise. The solution turned green and brown precipitate formed. The precipitate was collected by filtration, dried in vacuum, and is formulated as Mo₂(OPrⁱ)₆I₄ on the basis of its similar properties to the other Mo₂(OPrⁱ)₆X₄ compounds (X = Cl and Br). From the green hexane solution, green crystals have been obtained and these are the subject of continuing studies. The brown solids were thermally unstable and elemental analyses were not sought. ¹H nmr data for Mo₂(OPrⁱ)₆I₄ obtained in toluene-d₃ at 100 MHz, 22°C: δ = 1.07 (d, 12Hz), 2.00 (d, 6H), 5.72 (septet, 2H) and 7.90 (septet, 1H); J_{HH} = 7.0 Hz. δ in ppm relative to Me₄Si. I.r. data obtained from a Nujol mull between CsI plates in the range 200 - 1500 cm⁻¹: 250 m, 300 w, 402 m, 442 w, 456 m, 500 s, 590 m, 612 w, 640 s, 725 m, 830 s, 862 s, 898 s, 956 vs, 990 s, 1093 vs, 1134 m, 1168 m, 1308 s and 1340 w.

Thermal Stability of Mo₂(OPrⁱ)₆Br₄. A solid sample of Mo₂(OPrⁱ)₆Br₄ was heated in vacuo to 60°. The sample rapidly darkened with the evolution of a gas giving within 1 h a black molybdenum containing substance which was insoluble in all common organic solvents. The volatile product of this decomposition was identified as PrⁱBr.

Attempts to obtain a mass spectrum of $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ by the method of direct insertion yielded Pr^iBr^+ (m/e at 122 and 124) as the ion of high mass.

NMR tube samples of $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ in toluene- d_6 stored at ca. 0°C showed significant quantities of Pr^iBr . When heated to $+60^\circ\text{C}$ rapid decomposition occurred yielding black solids and Pr^iBr , which was identified by ^1H nmr spectroscopy.

Addition of $(\text{CD}_3)_2\text{CHBr}$ to a toluene- d_6 solution of $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ showed no exchange of isopropyl groups of the type shown below, which would be expected if elimination of Pr^iBr was reversible.



X-ray Structural Determinations. General operating procedures and computational techniques have been described previously.²⁷

$\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$. A crystal of dimensions $0.22 \times 0.18 \times 0.28$ mm was mounted in a nitrogen filled glove bag and transferred to the liquid nitrogen boil-off cold stream of the diffractometer. The cell dimensions from 30 reflections at -172° with MoK_α (λ 0.71069 \AA) were $a = 20.722(6) \text{ \AA}$, $b = 9.617(2) \text{ \AA}$, $c = 12.747(4) \text{ \AA}$, $\beta = 96.02(1)^\circ$, $V = 2922.6(1) \text{ \AA}^3$, $Z = 4$, $d_{\text{calcd.}} = 1.578$ and space group $\text{P}2_1/\text{a}$.

A total of 9983 reflections were collected including redundancies and reduced to 5175 unique amplitudes by using

standard moving-crystal moving-detector techniques with the following values: scan speed = 1.0 deg min^{-1} , scan width = $2.0 + \text{dispersion}$, single background time at extremes of scan = 5 s, aperture size = $3.0 \times 4.0 \text{ mm}$. The limits of data collection were $5^\circ < 2\theta < 50^\circ$. The number of reflections with $F > 2.33\sigma(F)$, based on counting statistics, was 4285. Due to the nearly uniform size of the crystal and low linear absorption coefficient ($\mu = 12.35 \text{ cm}^{-1}$) no absorption correction was applied.

The structure was solved using direct methods. Hydrogen atoms were apparent in a difference Fourier synthesis based on phases from the non-hydrogen atoms. Since several of the hydrogen atom parameters diverged upon refinement they were placed in idealized positions ($d_{C-H} = 0.95 \text{ \AA}$, $B_{iso} = 1 + B_{iso}$ of connected atom) and fixed during the final cycles of the full matrix refinement. The final residuals are: $R(F) = 0.0422$ and $R_w(F) = 0.0476$. The goodness of fit for the last cycle was 1.05 and the maximum Δ/σ was 0.05.

Several atoms located on the periphery of the molecule possess rather large anisotropic thermal parameters, the largest being C(17) with an isotropic equivalent²⁴ of 12.1 \AA^{-2} . These excessive parameters are attributed to thermal motion as opposed to disorder or sample decomposition, as evidenced by the facts that the hydrogen atoms were located in the course of refinement and four reflections chosen as standards and monitored during data collection exhibited only statistical

fluctuations. Errors based on the variance-covariance matrix are larger by nearly 50% for those atoms with "large" thermal parameters compared to errors not involving these atoms.

Mo₂(OPrⁱ)₆Br₄. Crystallization of Mo₂(OPrⁱ)₆Br₄ from toluene gave crystals which decrepitated upon drying in vacuo. Consequently, crystals were grown in toluene solution and a crystal was selected and taken directly from the mother liquor, to the goniostat using inert atmosphere handling techniques. The crystal dimensions were 0.08 X 0.20 X 0.48 mm. All data were collected at -171°C.

The cell dimensions obtained from 41 reflections at -171°C with MoK_α (λ 0.71069 Å) were a = 15.204(5) Å, b = 12.849(5) Å, c = 10.535(3) Å, β = 120.76(1)°, V = 1768.6(1) Å³, Z = 4, d_{calcd.} = 1.638 g cm⁻³ and space group P2₁/a.

A total of 4155 reflections were collected and reduced to 3134 unique amplitudes by using standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0 deg min⁻¹, scan width = 2.0 + dispersion, single background time at extremes of scan = 10 s, aperture size = 3.0 X 4.0 mm. The limits of data collection were 5° < 2θ < 50°. The number of reflections with F > 2.33σ(F), based on counting statistics, was 2618. The data were corrected for absorption: linear absorption coefficient = 51.92 cm⁻¹, with minimum and maximum corrections of 0.149 and 0.616, respectively.

The structure was solved using direct methods and lies

on a center of symmetry. A disordered solvent molecule was located and refined isotropically. (Details are given in the supplementary materials). All hydrogen atoms (other than those associated with the solvent molecule) were also located and refined. The final residuals are $R(F) = 0.0477$ and $R_w(F) = 0.0472$. The goodness of fit for the last cycle was 1.250 and the maximum Δ/σ was 0.05.

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Supplementary Data Available. Tables of observed and calculated structure factors (pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports 7928 and 7963 are available in microfiche form only from the Indiana University Library.

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Table 1. Fractional Coordinates for the $\text{Mo}_2\text{Cl}_4(\text{OPr}^i)_6$ Molecule

Atom	10^4x	10^4y	10^4z	$10B_{\text{iso}}$
Mo(1)	-1133.8(2)	3073.1(1)	3252.3(3)	20
Mo(2)	-1238.5(2)	1382.7(1)	1756.3(3)	17
Cl(3)	-642(1)	2934(1)	4813(1)	37
Cl(4)	-1458(1)	5385(1)	3660(1)	31
Cl(5)	-905(1)	-929(1)	1356(1)	24
Cl(6)	-1690(1)	1576(1)	181(1)	30
O(7)	-821(2)	1122(3)	3041(2)	24
C(8)	-451(3)	52(6)	3596(5)	44
C(9)	-842(4)	-1021(8)	3578(6)	64
C(10)	205(3)	-8(7)	3413(6)	55
O(11)	-1566(1)	3314(3)	1976(2)	21
C(12)	-1991(3)	4322(6)	1450(5)	37
C(13)	-2616(3)	4414(8)	1778(7)	65
C(14)	-1628(3)	5506(7)	1182(6)	49
O(15)	-1871(2)	2502(4)	3703(3)	36
C(16)	-2263(3)	2631(7)	4451(5)	49
C(17)	-2194(7)	1303(9)	4999(9)	121
C(18)	-2934(3)	2983(12)	4063(6)	94
O(19)	-386(1)	3898(3)	3013(2)	17
C(20)	91(2)	4930(5)	3336(3)	20
C(21)	725(2)	4187(6)	3626(4)	26
C(22)	141(2)	5970(5)	2583(4)	27
O(23)	-2001(2)	564(3)	1963(3)	27
C(24)	-2488(3)	-447(6)	1649(5)	36
C(25)	-2529(3)	-1512(7)	2391(6)	58
C(26)	-3113(3)	308(7)	1405(5)	44
O(27)	-486(1)	1958(3)	1351(2)	16
C(28)	-54(2)	1823(5)	650(3)	18
C(29)	599(2)	1356(6)	1095(4)	26
C(30)	-35(3)	3197(5)	173(4)	26

Note 1: The isotropic thermal parameter listed for those atoms refined anisotropically are the isotropic equivalent. Hamilton, W. C. Acta Crystallog. 1959, 12, 609.

Note 2: Numbers in parenthesis in this and all following tables refer to the error in the least significant digits.

Table 2. Bond Distances in Angstroms for the $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$ Molecule

A	B	Distance
Mo(1)	Mo(2)	2.731(1)
Mo(1)	Cl(3)	2.421(2)
Mo(1)	Cl(4)	2.416(1)
Mo(1)	O(7)	2.020(3)
Mo(1)	O(11)	2.013(4)
Mo(1)	O(15)	1.815(3)
Mo(1)	O(19)	1.808(3)
Mo(2)	Cl(5)	2.419(1)
Mo(2)	Cl(6)	2.419(2)
Mo(2)	O(7)	2.014(4)
Mo(2)	O(11)	2.016(3)
Mo(2)	O(23)	1.819(3)
Mo(2)	O(27)	1.814(3)
O(7)	C(8)	1.478(7)
O(11)	C(12)	1.472(6)
O(15)	C(16)	1.442(6)
O(19)	C(20)	1.446(5)
O(23)	C(24)	1.442(6)
O(27)	C(28)	1.442(5)
C(8)	C(9)	1.402(9)
C(8)	C(10)	1.414(9)
C(12)	C(13)	1.432(9)
C(12)	C(14)	1.443(8)
C(16)	C(17)	1.510(13)
C(16)	C(18)	1.486(12)
C(20)	C(21)	1.517(7)
C(20)	C(22)	1.506(7)
C(24)	C(25)	1.508(10)
C(24)	C(26)	1.496(8)
C(28)	C(29)	1.509(7)
C(28)	C(30)	1.500(7)

Table 3. Bond Angles in Degrees for the $\text{Mo}_2(\text{OPr}^i)_4\text{Cl}_2$ Molecule

A	B	C	Angle
Mo(2)	Mo(1)	Cl(3)	136.5(0)
Mo(2)	Mo(1)	Cl(4)	138.4(0)
Mo(2)	Mo(1)	O(7)	117.3(1)
Mo(2)	Mo(1)	O(11)	117.4(1)
Mo(2)	Mo(1)	O(15)	96.7(1)
Mo(2)	Mo(1)	O(19)	95.8(1)
Cl(3)	Mo(1)	Cl(4)	85.1(1)
Cl(3)	Mo(1)	O(7)	80.1(1)
Cl(3)	Mo(1)	O(11)	176.1(1)
Cl(3)	Mo(1)	O(15)	85.5(2)
Cl(3)	Mo(1)	O(19)	85.7(1)
Cl(4)	Mo(1)	O(7)	174.3(1)
Cl(4)	Mo(1)	O(11)	91.0(1)
Cl(4)	Mo(1)	O(15)	85.5(1)
Cl(4)	Mo(1)	O(19)	84.9(1)
O(7)	Mo(1)	O(11)	94.7(1)
O(7)	Mo(1)	O(15)	94.1(1)
O(7)	Mo(1)	O(19)	91.7(1)
O(11)	Mo(1)	O(15)	97.8(2)
O(11)	Mo(1)	O(19)	94.3(1)
O(15)	Mo(1)	O(19)	107.5(2)
Mo(1)	Mo(2)	Cl(5)	138.0(0)
Mo(1)	Mo(2)	Cl(6)	139.0(0)
Mo(1)	Mo(2)	O(7)	117.5(1)
Mo(1)	Mo(2)	O(11)	117.3(1)
Mo(1)	Mo(2)	O(23)	91.9(1)
Mo(1)	Mo(2)	O(27)	95.0(1)
Cl(5)	Mo(2)	Cl(6)	85.0(0)
Cl(5)	Mo(2)	O(7)	90.1(1)
Cl(5)	Mo(2)	O(11)	174.3(1)
Cl(5)	Mo(2)	O(23)	85.3(1)
Cl(5)	Mo(2)	O(27)	85.0(1)
Cl(6)	Mo(2)	O(7)	176.1(1)
Cl(6)	Mo(2)	O(11)	88.8(1)
Cl(6)	Mo(2)	O(23)	85.5(1)
Cl(6)	Mo(2)	O(27)	85.1(1)
O(7)	Mo(2)	O(11)	91.8(1)
O(7)	Mo(2)	O(23)	94.8(2)
O(7)	Mo(2)	O(27)	92.8(1)
O(11)	Mo(2)	O(23)	93.3(1)
O(11)	Mo(2)	O(27)	95.1(1)
O(23)	Mo(2)	O(27)	168.2(1)
Mo(1)	O(7)	Mo(2)	85.2(1)
Mo(1)	O(7)	C(8)	135.9(4)
Mo(2)	O(7)	C(8)	139.0(4)

Table 3. Bond Angles in Degrees for the $\text{Mo}_2(\text{OPr}^i)_6\text{Cl}_4$ Molecule
(continued)

Mo(1)	O(11)	Mo(2)	85.3(1)
Mo(1)	O(11)	C(12)	138.7(3)
Mo(2)	O(11)	C(12)	135.7(3)
Mo(1)	O(15)	C(16)	144.8(4)
Mo(1)	O(19)	C(20)	143.8(3)
Mo(2)	O(23)	C(24)	146.0(3)
Mo(2)	O(27)	C(28)	145.9(3)
O(7)	C(8)	C(9)	113.2(6)
O(7)	C(8)	C(10)	112.0(5)
C(9)	C(8)	C(10)	128.6(6)
O(11)	C(12)	C(13)	111.9(5)
O(11)	C(12)	C(14)	111.5(5)
C(13)	C(12)	C(14)	124.0(6)
O(15)	C(16)	C(17)	107.9(5)
O(15)	C(16)	C(18)	107.7(6)
C(17)	C(16)	C(18)	115.6(8)
O(19)	C(20)	C(21)	108.1(4)
O(19)	C(20)	C(22)	108.1(4)
C(21)	C(20)	C(22)	113.3(4)
O(23)	C(24)	C(25)	108.4(5)
O(23)	C(24)	C(26)	108.0(4)
C(25)	C(24)	C(26)	113.0(5)
O(27)	C(28)	C(29)	108.1(4)
O(27)	C(28)	C(30)	107.8(4)
C(29)	C(28)	C(30)	113.6(4)

Table 4. Fractional Coordinates for the $\text{Mo}_2(\text{OPr}^i)_6\text{Br}_4$ Molecule

Atom	10^4x	10^4y	10^4z	$10B_{\text{iso}}$
Mo(1)	-54.1(4)	-614.4(5)	8900.2(1)	11
Br(2)	1144(1)	-1445(1)	8117(1)	19
Br(3)	-1471(1)	-1523(1)	6560(1)	23
O(4)	-1124(3)	-41(4)	9295(5)	12
C(5)	-2261(5)	-91(6)	8497(8)	15
C(6)	-2691(7)	981(8)	8009(9)	23
C(7)	-2587(6)	-654(7)	9424(9)	21
O(8)	-185(4)	445(4)	7691(5)	14
C(9)	-358(6)	775(6)	6245(8)	18
C(10)	539(8)	1427(8)	6499(10)	25
C(11)	-1375(7)	1317(8)	5453(10)	28
O(12)	60(4)	-1840(4)	9834(5)	15
C(13)	44(7)	-2949(6)	9787(9)	23
C(14)	1010(9)	-3342(8)	11102(11)	35
C(15)	-918(11)	-3337(8)	9725(18)	39

Table 5. Bond Distances in Angstroms for the $\text{Mo}_2(\text{OPr}^i)_4\text{Br}_4$ Molecule

A	B	Distance
Mo(1)	Mo(1)'	2.739(1)
Mo(1)	Br(2)	2.584(1)
Mo(1)	Br(3)	2.579(1)
Mo(1)	O(4)'	2.012(4)
Mo(1)	O(4)	2.014(4)
Mo(1)	O(8)	1.805(5)
Mo(1)	O(12)	1.818(5)
O(4)	C(5)	1.487(8)
O(8)	C(9)	1.470(8)
O(12)	C(13)	1.426(9)
C(5)	C(6)	1.499(11)
C(5)	C(7)	1.490(10)
C(9)	C(10)	1.504(11)
C(9)	C(11)	1.501(11)
C(13)	C(14)	1.500(14)
C(13)	C(15)	1.515(13)

Table 6. Bond Angles in Degrees for the $\text{Mo}_2(\text{OPr}^i)_8\text{Br}_4$ Molecule

A	B	C	Angle
Mo(1)	Mo(1)	Br(2)	139.6(0)
Mo(1)	Mo(1)	Br(3)	136.8(0)
Mo(1)	Mo(1)	O(4)	47.2(1)
Mo(1)	Mo(1)	O(4)	47.1(1)
Mo(1)	Mo(1)	O(8)	95.7(1)
Mo(1)	Mo(1)	O(12)	95.4(1)
Br(2)	Mo(1)	Br(3)	83.6(0)
Br(2)	Mo(1)	O(4)	92.4(1)
Br(2)	Mo(1)	O(8)	173.3(1)
Br(2)	Mo(1)	O(12)	85.8(1)
Br(2)	Mo(1)	O(4)	85.8(1)
Br(3)	Mo(1)	O(4)	176.0(1)
Br(3)	Mo(1)	O(8)	89.7(1)
Br(3)	Mo(1)	O(12)	86.0(2)
Br(3)	Mo(1)	O(4)	85.8(2)
O(4)	Mo(1)	O(4)	94.3(2)
O(4)	Mo(1)	O(8)	93.5(2)
O(4)	Mo(1)	O(8)	94.3(2)
O(4)	Mo(1)	O(12)	93.9(2)
O(4)	Mo(1)	O(12)	93.4(2)
O(8)	Mo(1)	O(12)	168.9(2)
Mo(1)	O(4)	Mo(1)	85.7(2)
Mo(1)	O(4)	C(5)	134.0(4)
Mo(1)	O(4)	C(5)	140.2(4)
Mo(1)	O(8)	C(9)	147.7(4)
Mo(1)	O(12)	C(13)	148.4(5)
O(4)	C(5)	C(6)	109.3(6)
O(4)	C(5)	C(7)	109.3(6)
C(6)	C(5)	C(7)	116.0(7)
O(8)	C(9)	C(10)	108.1(6)
O(8)	C(9)	C(11)	107.3(6)
C(10)	C(9)	C(11)	115.0(8)
O(12)	C(13)	C(14)	108.2(7)
O(12)	C(13)	C(15)	109.2(7)
C(14)	C(13)	C(15)	113.4(9)

Captions to Figures

Figure 1. An ORTEP view of the $\text{Mo}_2\text{Cl}_4(\text{OPr}^i)_6$ molecule showing the atom numbering scheme used in the Tables. The hydrogen atoms have been omitted for clarity; atoms are drawn at the 40% probability level.

Figure 2. An ORTEP view of the $\text{Mo}_2\text{Br}_4(\text{OPr}^i)_6$ molecule showing the atom numbering scheme used in the Tables. Atoms are drawn at the 40% probability level. Hydrogen atoms have been omitted for clarity.

